Bis(trimethylsilyl)benzamidinate

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Published in:
Journal of the American Chemical Society

DOI:
10.1021/ja00064a081

Publication date:
1993

Bis(trimethylsilyl)benzamidinate: A Promising Spectator Ligand in Organoyttrium Chemistry. Synthesis and Reactivity of $\{[C_6H_5C(NSiMe_3)_2]_2Y\text{-}\mu\text{-}R\}_2$ (R = H, C≡CH) and X-ray Structure of $\{[C_6H_5C(NSiMe_3)_2]_2Y\text{-}\mu\text{-}C{\equiv}CH\}_2$

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Received January 22, 1993

Permethylyttrocene alkyl and hydrido derivatives $Cp^*_2Y\text{–}R$ ($Cp^* = \eta^5\text{-}C_5Me_5$; R = H, $CH(SiMe_3)_2$) are effective catalysts for a variety of reactions.[1] Previously we have found that Cp^*_2LnR (Ln = Y, La, Ce; R = $CH(SiMe_3)_2$) catalyzes, for instance, the oligomerization of terminal alkynes.[1a,2] We were interested in exploring yttrium-based systems with an alternative coordination environment and comparing these with the known chemistry. We have chosen the bidentate *N,N'*-bis(trimethylsilyl)benzamidinate ligand, earlier employed by Roesky,[3] Dehnicke[4] and Edelmann,[5] to develop new catalytic group 3 chemistry for C-C and C-H bond formation.

Here we describe the preparation of bis(*N,N'*-bis(trimethylsilyl)benzamidinate)yttrium hydride, $\{[C_6H_5C(NSiMe_3)_2]_2Y\text{-}\mu\text{-}H\}_2$, and its use as a precursor in the catalytic dimerization of terminal alkynes, together with the synthesis and crystal structure of the novel acetylide complex $\{[C_6H_5C(NSiMe_3)_2]_2Y\text{-}\mu\text{-}C{\equiv}CH\}_2$.

Multigram quantities of the chloride complex $[C_6H_5C(NSiMe_3)_2]_2YCl{\cdot}THF$ (**1**)[7a] can be easily obtained by reaction of $Li[C_6H_5C(NSiMe_3)_2]$[6] with $YCl_3{\cdot}THF_{3.5}$.[7b] The chloride is an excellent precursor to new yttrium alkyl complexes.[8] For instance, reaction of **1** with $LiCH(SiMe_3)_2$ afforded salt-free $[C_6H_5C(NSiMe_3)_2]_2YCH(SiMe_3)_2$ (**2**).[7b] The proton-coupled ^{13}C NMR spectrum of **2** shows a double doublet from the methyne carbon at δ 43.5 ($^1J_{Y\text{-}C}$ = 30 Hz, $^1J_{C\text{-}H}$ = 88 Hz), which is shifted significantly downfield from the C-H resonance in $Cp^*_2YCH(SiMe_3)_2$ (δ 25.2),[9] suggesting a more electrophilic yttrium environment in **2**. Like in $Cp^*_2YCH(SiMe_3)_2$ ($^1J_{C\text{-}H}$ = 84 Hz),[9] the small coupling constant for the α-carbon resonance ($^1J_{C\text{-}H}$ = 88 Hz) indicates an agostic interaction[10] of the alkyl C-H bond with yttrium as is expected for an electronically very unsaturated compound (14 electron system at maximum). Treatment of **2** with dihydrogen (3 atm, 40 °C) in benzene gives the very air-sensitive hydride $\{[C_6H_5C(NSiMe_3)_2]_2Y\text{-}\mu\text{-}H\}_2$ (**3**).[7b] The ^1H NMR spectrum of **3** shows a triplet at 8.3 ppm ($^1J_{Y\text{-}H}$ = 27.6 Hz), which suggests a symmetric dimeric structure in solution.[11] None of the synthesized complexes (**1**–**3**) shows any disproportionation or decomposition after 24 h at 100 °C in benzene, demonstrating the high stability of this new class of yttrium compounds.

With **3** available, we were interested in examining the reactivity with terminal alkynes, and making comparisons with the bis(permethylcylopentadienyl) analogues of yttrium, lanthanum, and cerium. Treatment of **3** with an excess of HC≡CR (R = *t*-Bu, Ph) gives a slow but selective reaction affording the head-to-tail coupled product $H_2C{=}C(R)C{\equiv}CR$ (R = *t*-Bu, Ph).[12] However, for $HC{\equiv}CSiMe_3$, a dramatic change in regioselectivity takes place and catalytic dimerization to exclusively the head-to-head coupled product *trans*-$R(H)C{=}C(H)C{\equiv}CR$ (R = $SiMe_3$) is observed.[12,13] By contrast, the Cp^*_2LnR-catalyzed coupling of HC≡CPh and $HC{\equiv}CSiMe_3$ gives either mixtures of head-to-tail and head-to-head isomers (Ln = Y) or formation of higher oligomers (Ln = La, Ce).[2] The mechanism for this reaction is believed to be the same as for the catalytic dimerization of terminal alkynes by Cp^*_2LnR (Ln = Sc, Y, La, Ce).[1a,2,14] Unlike Cp^*_2ScMe,[15] **3** does not oligomerize ethyne. Treating **3** with an excess of ethyne resulted in the formation of an acetylide.[7b] An X-ray structure determination revealed the compound to be $\{[C_6H_5C(NSiMe_3)_2]_2Y\text{-}\mu\text{-}C{\equiv}CH\}_2$ (**4**), a dimer with bridging ethynyl groups. **4** was also prepared by treatment of **2** with ethyne in benzene (eq 1).[7b]

$$2[C_6H_5C(NSiMe_3)_2]_2Y\text{–}R + HC{\equiv}CH \rightarrow \{[C_6H_5C(NSiMe_3)_2]_2Y\text{-}\mu\text{-}C{\equiv}CH\}_2 + RH \quad (1)$$

R = $CH(SiMe_3)_2$ (**2**), H (**3**); (**4**)

An ORTEP drawing of **4** is shown in Figure 1. The unit cell contains two crystallographically independent molecules, both obeying C_2 symmetry, that do not differ markedly in their structures.[16] In one molecule, two identical $[C_6H_5C(NSiMe_3)_2]_2Y\text{—}C{\equiv}CH$ units are related to each other by a 2-fold axis perpendicular to the plane of the acetylide bridge. In the other molecule, the two yttrium atoms are on a special position along the 2-fold axis, with disordered acetylide fragments. Notable features of the nondisordered molecule will be discussed

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(16) Crystal data for **4**: $(C_{28}H_{47}N_4Si_4Y)_2$, space group $C2/c$ with a = 27.088(2), b = 27.102(2), and c = 20.964(1) Å, β = 113.40(1)°, V = 14125(2) Å^3, d_{calcd} = 1.206 g cm^{-3}, and Z = 8. Data were collected on an Enraf–Nonius CAD-4F diffractometer at 130 K with Mo Kα (λ = 0.710 73 Å). The structure was solved by Patterson methods and refined to $R(F)$ = 0.044, $R_w(F)$ = 0.036, for 7813 unique reflections with $I \geq 2.5\ \sigma(I)$ and 1035 parameters.

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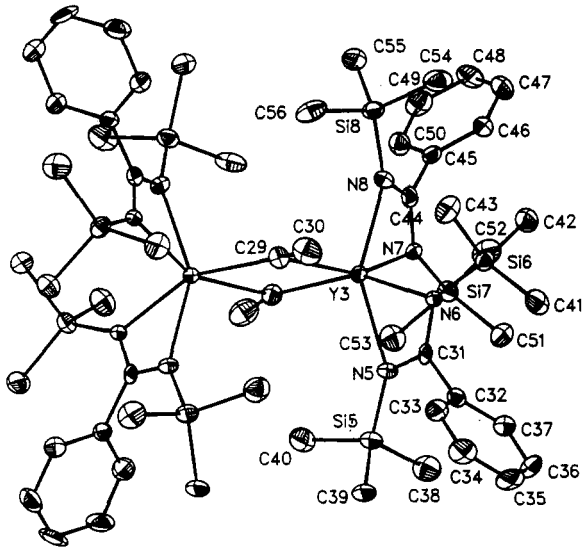

Figure 1. ORTEP drawing of $\{[C_6H_5C(NSiMe_3)_2]_2Y\text{-}\mu\text{-}C{\equiv}CH\}_2$ (**4**). Only one of the crystallographically independent molecules is shown with 50% probability ellipsoids.

here (Figure 1). **4** is formed by two distorted octahedral yttrium atoms, each coordinated by two chelating benzamidinate ligands and two bridging acetylides. Due to a *trans*-effect, the Y(3)-N(5) (2.395(4) Å) and Y(3)-N(8) (2.381(4) Å) bond lengths are longer than Y(3)-N(6) (2.345(4) Å) and Y(3)-N(7) (2.335(4) Å) (*trans* to the acetylide). The Y(3)-C(29) (2.556(5) Å) and Y(3)a-C(29) (2.509(5) Å) bonds are longer than in $Cp^*_2Y(\mu\text{-}C{\equiv}CCMe_3)_2Li{\cdot}THF$ (2.38(2) Å)[17a] but very similar to the Y-C distances in $[Cp_2Y\text{-}\mu\text{-}Me]_2$ (2.553(1), 2.537(9) Å).[17b] The Y-C bond lengths of **4** compare well with the Ln-C distances of some 4f element acetylide complexes, $[Cp'_2Ln\text{-}\mu\text{-}C{\equiv}CR]_2$ (Cp' = substituted cyclopentadienyl, Ln = Sm, Er) when the differences in atomic radii are taken into account.[18] A remarkable feature is that, in contrast to the Cp^*_2Ln (Ln = La, Ce,[19a] and Sm[19b]) systems, no coupling of acetylide fragments is observed. Both the Y(3)-C(29) and Y(3)a-C(29) bond lengths and the Y(3)-C(29)-C(30) (98.4(5)°) and Y(3)a-C(29)-C(30) (159.8(5)°) angles indicate that the bridge is clearly asymmetric with a strong interaction of the α-carbon atom, C(29), with both yttrium centers. The acetylide absorption (ν(C≡C) 1915 cm^{-1}) in the IR spectrum (cf. ν(C≡C) ($Cp_3UC{\equiv}CH$) 2062 cm^{-1}),[20] the $^1J_{C\text{-}H}$ coupling constant for $YC{\equiv}CH$ of 218 Hz in the ^{13}C NMR spectrum, and the Y(3)a-C(29)-C(30) angle of 159.8(5)° suggest η^2 interaction of the triple-bond π orbitals with Y(3).[18a] Since π interaction of the acetylide is expected to result in elongation of the C≡C bond, the C(29)-C(30) bond length of 1.164(8) Å, shorter than that in free acetylene (1.21 Å), is very surprising.

These preliminary results show that the *N,N'*-bis(trimethylsilyl)benzamidinate acts as an inert spectator ligand in these complexes. The thermal stability and catalytic activity of **3** clearly demonstrate that a much more diverse chemistry is available to yttrium than that of cyclopentadienyl systems only. Indeed, exploratory experiments showed that the hydride $\{[C_6H_5C(NSiMe_3)_2]_2Y\text{-}\mu\text{-}H\}_2$ (**3**) also polymerizes ethene under mild conditions. These promising perspectives for catalytic C-H and C-C bond formation are currently under investigation.

Acknowledgment. This work was financially supported by Shell Research B.V., which is gratefully acknowledged.

Supplementary Material Available: Full experimental details; spectroscopic and analytical data; ORTEP drawings; tables of crystal data, anisotropic thermal displacement parameter atomic coordinates, bond lengths, bond angles and torsion angles (33 pages); list of observed and calculated structure factors (60 pages). Ordering information is given on any current masthead page.

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